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(54) Crystalline aluminosilicate
catalyst

(57) A novel crystalline aluminosilicate of the erionite type wherein barium ions occupy at least part of the sites of the exchangeable cations of the crystal lattice, has useful properties in the preparation of olefins, in particular ethene, by contacting methanol and/or dimethyl ether with a catalyst comprising said aluminosilicate.

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SPECIFICATION

Crystalline aluminosilicate and preparation thereof, catalytic composition and process for the preparation of olefins and olefins thus prepared

- 5 This application relates to a crystalline aluminosilicate of the erionite type, to its preparation, to its use in the preparation of olefins and to the olefins thus prepared. 5
- Erionite is a naturally occurring aluminosilicate of the zeolite family. Its physical and chemical properties, as well as a process for the preparation of a synthetic erionite material, and its use as a catalyst, are described in an article entitled "Synthetic Erionite and Selective Hydrocracking" ("Molecular Sieve Zeolites 10 II", Advances in Chemistry Series 102 (1971) pp. 417-425). As indicated by the title, it is proposed in that article to use erionite in hydrocracking processes. Thus naphtha (pentane/hexane) can be converted into C₄-gas, mainly propane. As those in the art are aware, there exists only a limited interest in the manufacture of lower alkanes. However, it is much more attractive to be able to manufacture (from cheap feedstocks) e.g. 15 lower olefins, for molecules like ethene and propene are building blocks and starting materials for many important chemical products. 15
- The Applicant has now found that when methanol and/or dimethyl ether are passed over a catalyst containing a novel crystalline aluminosilicate of the erionite type, olefins are produced in good yield. The novelty of the present erionite resides in the fact that it contains barium ions instead of the cations usually 20 present therein, i.e. potassium and sodium. 20
- The invention therefore relates to a crystalline aluminosilicate of the erionite type, characterized in that barium ions occupy at least part of the sites of the exchangeable cations of the crystal lattice.
- The present barium-erionites enable the production of ethene and other olefins to proceed in surprisingly high yield. Other erionites, including cation-exchanged and non-exchanged materials, also appear to 25 catalyse the reaction from methanol to olefins, but with substantially lower yields, and with high to very high coke makes. The deposition of coke on the catalytic material gradually lowers its activity and necessitates frequent regenerations. The use of barium-erionite, however, results in very low coke makes and relatively long catalyst life times, therefore. 25
- The barium ions occupy at least part of the sites of the exchangeable cations of the crystal lattice. As those 30 in the art are aware, crystalline aluminosilicates may contain cations which can be exchanged for other cations, and so does erionite: the sodium and potassium monovalent ions can be replaced by other monovalent ions, e.g. hydrogen, ammonium, tetraalkylammonium or other alkali metals, or by (half the molar quantity of) bivalent ions, e.g. barium, strontium, zinc and the like. Replacement with barium ions has not been proposed or performed up to now, and its remarkable catalytic properties in the conversion of 35 methanol to olefins are unexpected. 35
- Very good results are obtained when the barium ions occupy at least 25%, particularly at least 50%, of the sites of the exchangeable cations of the crystal lattice. The upper limit, of course, is 100%, but in practice this limit is almost never completely arrived at. Moreover, already when the barium ions occupy about 70% of the sites of the exchangeable cations, excellent catalytic properties are reached.
- 40 It is conceivable to synthesize the present erionite from reactants already containing barium instead of sodium and potassium; it is preferred however to synthesize (or buy) normal erionite, having sodium and potassium ions, and to replace those ions with barium ions, applying ion-exchange techniques known per se. Thus the present invention also relates to a process for the preparation of the crystalline aluminosilicate according to the invention, characterized in that a crystalline aluminosilicate of the erionite type is subjected 45 to an ion-exchange treatment with barium ions. 45
- Suitably a sodium and potassium containing erionite is contacted with a solution of a barium salt, preferably the nitrate, in large excess and/or in several steps. After solvent evaporation and drying, the exchanged erionite is preferably calcined, for instance at a temperature between 300 and 600°C for a period of 15 minutes to four hours. The amount and the concentration of the barium solution are chosen such that 50 the final product contains the desired quantity of barium ions. Conveniently concentrations of 0.01 to 1 M are used. 50
- The crystalline aluminosilicates of the invention may be incorporated with another material resistant to the temperature and other conditions employed in organic conversion processes. Such materials - hereinafter called "binders" - include active and inactive materials and synthetic or naturally occurring zeolites as well 55 as inorganic materials such as clays, silica and/or metal oxides. The purpose of this incorporation may be to improve e.g. the crushing strength or the attrition resistance, or also to regulate the catalytic properties, e.g. as a diluent, so that products can be obtained in an orderly manner without employing other means for controlling the rate of reaction. The invention also relates therefore to a catalytic composition, in particular for the preparation of olefins, comprising the crystalline aluminosilicate according to the invention and a 60 binder therefor. 60
- Since the present aluminosilicate can be used with advantage in the preparation of lower olefins, the invention also relates to a process for the preparation of olefins, in particular ethene, by contacting methanol and/or dimethyl ether with a catalyst comprising a crystalline aluminosilicate or a composition as described hereinbefore. The use of methanol as a starting material more or less includes the use of dimethyl ether, for 65 the formation of ethene can be viewed as a combination of two reactions: first, a condensation of methanol 65

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to dimethyl ether, and secondly, a dehydration of this ether to yield ethene. However, other reaction mechanisms are conceivable, and the Applicant does not wish to be limited by the theory given above.

The methanol and/or the dimethyl ether are suitably contacted with the catalyst under conversion conditions including a temperature in the range of 300 to 550°C, a gaseous hourly space velocity of 100 to 10000 1/1/h, and a pressure in the range of 0.1 to 30 bar, preferably atmospheric pressure. Carrier gases or diluents may be injected into the reaction zone, such as nitrogen, helium or steam.

The conversion process may be carried out as a batch-type, semi-continuous or continuous operation utilizing a fixed, fluidized or moving bed catalyst system. A preferred embodiment entails use of a catalyst zone wherein the alcohol or ether charge is passed concurrently or countercurrently through a fluidized or moving bed of particle-form catalyst. The latter after use is conducted to a regeneration zone wherein coke is burned from the catalyst in an oxygen-containing atmosphere, e.g. air, at an elevated temperature, after which the regenerated catalyst is recycled to the conversion zone for further contact with the alcohol and/or ether feed.

The product stream in the process according to the invention contains steam and a hydrocarbon mixture of paraffins and olefins, substantially devoid of aromatics. This mixture is particularly rich in lower olefins, i.e. ethene and propene. Generally, a major fraction of the total olefins production is ethene plus propene, with the ethene content of the product exceeding the propene content. Thus, the predominant hydrocarbon product constitutes valuable petrochemicals. The steam and hydrocarbon products may be separated from one another by methods well known in the art.

In a preferred embodiment of the reaction, the unconverted methanol and/or dimethyl ether, are recycled to the reaction zone.

The following example illustrates the invention.

Example

A. Catalysts were prepared from commercially obtained Na-erionite. The X-ray diffraction pattern of the Na-erionite agreed closely with the literature values of pure, 100% crystalline erionite, including the sharp "1" odd lines (observed at about 9.7, 16.6, 21.4 and 31.9° 2θ) which are forbidden for the - related - offretite structure.

The Na-erionite was converted into the ammonium form by boiling the material in a 1 M NH_4NO_3 aqueous solution. The hydrogen form was prepared herefrom by calcining at 500°C for three hours. The metal exchanged forms were prepared from Na-erionite by ion-exchange at room temperature for 48 hours using a large excess of a 0.1 M aqueous solution of the corresponding nitrate. After solvent evaporation and drying at 120°C for 16 hours, the exchanged erionites were pressed into tablets, ground and sieved to 180-600 μm, and calcined at 450°C for one hour. X-ray diffraction of the final materials showed the same crystallinity as before the ion-exchanges.

The following exchanged erionites were thus prepared, of which only Ba-erionite is according to the invention. For further comparison also a barium-exchanged mordenite was prepared.

1. H^+ -erionite, containing 1.7 g Na/100 g, corresponding to 77% (molar) exchange
2. Mg^{2+} -erionite, containing 2.5 g Mg/100 g, corresponding to 64% (molar) exchange.
3. Zn^{2+} -erionite, containing 7.2 g Zn/100 g, corresponding to 71% (molar) exchange
4. Fe^{2+} -erionite, containing 3.5 g Fe/100 g, corresponding to 40% (molar) exchange
5. Mn^{2+} -erionite, containing 5.9 g Mn/100 g, corresponding to 69% (molar) exchange
6. Ba^{2+} -erionite, containing 13.8 g Ba/100 g, corresponding to 70% (molar) exchange
7. Ba^{2+} -mordenite, containing 9.6 g Ba/100 g, corresponding to 65% (molar) exchange

B. The aluminosilicates prepared above were tested for their catalytic activity in a fixed bed, atmospheric flow reactor system. In each experiment 5 ml of aluminosilicate was brought into the reactor. A mixture of methanol, steam and helium (volumetric ratio 1:2:3) was pumped into the reactor via a preheater. The product gases leaving the reactor were passed through a cold trap to remove CH_3OH , H_2O and other condensable gases. The remaining gases were analyzed by a dual GLC-system equipped with a flame-ionization and a thermal conductivity detector. The reaction conditions were 400°C, 1 bar and a GHSV of 700 1/1/h. The results are tabulated below. The conversion was 100% in all experiments. The selectivities listed are the values obtained after averaging over the catalyst's life time and are expressed as carbon efficiencies (= mole C in product/mole C in methanol feed).

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	Catalyst	total olefins	ethene	alkanes	coke	life time, h	
	1	27	16	44	29	5	
5	2	33	20	38	29	6	
	3	43	26	32	25	7.5	5
	4	44	26	36	20	10	
	5	46	28	33	21	11	
	6	79	40	17	4	36	
10	7	51	23	35	14	19	10

Evidently, catalyst 6, barium-erionite, is most selective towards olefins and ethene formation, and accumulates the least amount of coke, thereby having the longest life time.

A detailed analysis of the gases resulting from the use of barium-erionite is given below (again selectivities expressed as carbon efficiencies):

	CH ₄	4%	
	C ₂ H ₄	40%	
	C ₂ H ₆	1%	
20	C ₃ H ₆	31%	20
	C ₃ H ₈	6%	
	1,2- C ₄ H ₈	4%	
	iso- C ₄ H ₈	3%	
	C ₄ H ₁₀	3%	
25	C ₅ H ₁₀	1%	25
	C ₅ H ₁₂	3%	

C. Regeneration of the catalysts proved feasible. For instance, after passing a helium stream, containing 1 %v O₂, over a catalyst, with the temperature rising from 20°C to 500°C in 4 hours, followed by a final treatment for 30 minutes at 500°C using helium containing 5 %v O₂, all the coke had been removed from the catalyst. The performance of the regenerated catalyst was identical with the performance of a freshly prepared one.

CLAIMS

1. Crystalline aluminosilicate of the erionite type, characterized in that barium ions occupy at least part of the sites of the exchangeable cations of the crystal lattice.
2. A crystalline aluminosilicate as claimed in claim 1, characterized in that the barium ions occupy at least 25% of the sites of the exchangeable cations of the crystal lattice.
3. Process for the preparation of the crystalline aluminosilicate as claimed in either of claims 1 or 2, characterized in that a crystalline aluminosilicate of the erionite type is subjected to an ion-exchange treatment with barium ions.
4. Catalytic composition, in particular for the preparation of olefins, comprising the crystalline aluminosilicate as claimed in either of claims 1 or 2, and a binder therefor.
5. Process for the preparation of olefins, in particular ethene, by contacting methanol and/or dimethyl ether with a catalyst comprising a crystalline aluminosilicate as claimed in claims 1 or 2 or a composition as claimed in claim 4.
6. A process as claimed in claim 5, characterized in that the methanol and/or the dimethyl ether are contacted with the catalyst under conversion conditions including a temperature in the range of from 300 to 550°C, a gaseous hourly space velocity in the range of from 100 to 10000 1/h, and a pressure in the range of from 0.1 to 30 bar.
7. Olefins, in particular ethene, whenever prepared by a process as claimed in claims 5 or 6.
8. Process for the preparation of the crystalline aluminosilicate as claimed in claim 3, substantially as described hereinbefore with particular reference to the example.
9. Process for the preparation of olefins as claimed in claim 5, substantially as described hereinbefore with particular reference to the example.